Supporting Information for:

Hydrogen Evolution with Minimal Parasitic Light Absorption by Dense Co-P Catalyst Films on Structured p-Si Photocathodes

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Experimental Details

Materials: 100mm P-type Si <100> wafers with a thickness of 525 μm and resistivity of 10-20 Ω-cm were obtained from Addison Engineering. All chemicals were commercially available and used as received. Cobalt(II) chloride hexahydrate ($CoCl_2$, >99.9%) was obtained from Alfa Aesar, whereas sodium hypophosphite monohydrate ($NaPO_2H_2$), boric acid (H_3BO_3, >99.5%), concentrated ammonium hydroxide (NH_4OH, ACS reagent 28%-30%) and potassium hydroxide (KOH, 99.99%) were obtained from Sigma-Aldrich. Buffered oxide etchant (6:1 (v/v) 40% NH_4F to 49% HF) was obtained from Transene Inc. Sodium chloride (NaCl, 99%) and hydrogen peroxide (H_2O_2, ACS grade 30%) were obtained from Macron Chemicals. TraceMetal grade sulfuric acid (H_2SO_4) was obtained from Fisher Scientific and diluted to 0.50 M with water with a resistivity of 18.2 MΩ·cm, obtained from a Millipore deionized (DI) water system.

Preparation of Si Photocathodes: Si was structured into microwire arrays via deep reactive ion etching, RIE, of a wafer that was patterned with an array of >120 nm thick Al_2O_3 masks with diameter 3 μm and a pitch of 7 μm. Shipley 1813 photoresist was spin coated onto a degreased wafer at 4000 RPM for 30 s and a pattern was defined using UV exposure through a chrome

mask. The pattern was developed with MF-319 developer and the resist was hard-baked at 115 °C for 10 minutes. The Al_2O_3 was deposited via E-Beam evaporation at 1 Å s^{-1}. Etching of the Si was performed using a SF_6/O_2 plasma controlled by an Oxford DRIE 100 ICP-RIE system at -130 °C. An ICP power of 900 W produced fast etching rates while a low CCP power of 3 W kept the energy of ions low and minimized sidewall damage. Randomly textured micropyramid, μP, substrates were formed via anisotropic etching of an unpatterned Si wafer that was first cleaned in 3:1 H_2SO_4 to 30% wt H_2O_2 for 10 min. Etching was performed in an aqueous solution of 2% wt potassium hydroxide/20% v isopropyl alcohol that was heated in a water bath at 80 °C for 1 h.[1] All Si samples were cleaned in a RCA SC1 bath (5:1:1 $H_2O/NH_4OH/H_2O_2$, 80 °C for >10 min), buffered oxide etch (at room temperature for 5 min), and a RCA SC2 bath (6:1:1 $H_2O/HCl/H_2O_2$, 70°C for >10 min) to remove SiO_2, Al_2O_3 and trace metal impurities. An n^+p junction was formed via diffusion doping with CeP_2O_{14} doping wafers (Saint-Gobain, PH-900 PDS) at 850 °C for 10 min. The P_2O_5 glass was removed from the Si surface by etching in BOE for > 60 s.

Electrode Fabrication: Samples were cleaved with a carbide scribe into ~10 mm^2 chips, and Ga/In eutectic was scratched into the back of the electrodes along with Ag paint (Ted Pella) to attach the electrodes to a Sn-coated Cu wire. The back contact and sides of the electrodes were sealed to 6 mm outer diameter glass tubing using insulating epoxy (Loctite 9460), and the epoxy which was cured for at least 12h. Care was taken to ensure the epoxy did not substantially mask the face of the electrode, so that the electrochemically active area was very similar to the photoactive area of the electrode.

Deposition and Testing of Si/Co-P devices: Prior to testing, devices were cleaned in 0.50 M sulfuric acid and surficial SiO_2 was removed in buffered oxide etch; planar and micropyramid

samples were etched in BOE for 10 s and microwire samples were etched in BOE for 30 s. Silicon photocathodes were decorated with Co-P catalyst films via a low-temperature, scalable photoelectrochemical deposition process.[2] Depositions and testing were controlled with a BioLogic SP-200 potentiostat. A saturated calomel electrode (SCE) was used as a reference and the counter electrode was a high-purity graphite rod (Alfa Aesar, 5N). The illumination source was a Thorlabs narrowband light-emitting diode with intensity averaged peak wavelength of 625 nm, tuned to a power density of 170 mW cm^{-2}. Co-P was deposited potentiostatically until the desired charge-density had passed, normalized to the projected area of the electrode. Catalyst loadings were therefore normalized with respect to the irradiance to provide a comparison of the amount of catalyst in the path of the light, as opposed to with respect to the density of catalyst on the surface of the features on the microstructured electrode (Figure S1). The potential of the p and n^+p working electrodes were held at -1.2V and -0.8 V vs SCE, respectively, to obtain optimum catalyst performance. For the planar and μW n+-Si devices, Co-P was deposited potentiostatically at -1.3V under dark conditions with rapid stirring near the working electrode.

Testing of the Si/Co-P photocathodes using a three-electrode set up was performed immediately after depositions in a 0.50 M H_2SO_4(aq) electrolyte continuously purged with H_2(g). A Ag/AgCl/(3.0 M KCl) electrode was used as the reference electrode. A high-purity graphite rod counter electrode was kept behind a glass frit to prevent oxygen or dissolved carbon species from reaching the working electrode. Solar simulation was provided from a Xe arc lamp equipped with an AM 1.5 filter and a liquid filter to remove excess IR illumination. The light intensity was adjusted so that a calibrated Si reference diode (Thorlabs FDS100) produced the photocurrent predicted for illumination under 100 mW cm^{-2} of the AM1.5 spectrum. A bare p-Si photoelectrochemical diode was used as an internal standard and exhibited a light limited

photocurrent density of ~28 mA cm^{-2}. Cyclic voltammograms were recorded at 50 mV s^{-1} with no IR-compensation. After testing, samples were immediately removed from the cell, rinsed with H_2O and dried in a stream of N_2(g), before further characterization.

Characterization: Scanning-electron micrographs (SEMs) were obtained with an FEI Nova NanoSEM 450 at an accelerating voltage of 10.00 kV and a working distance of 5.00 mm using an Everhart-Thornley secondary electron detector. Energy-Dispersive X-Ray spectra were obtained at an accelerating voltage of 15.00 kV.

Supporting Figures

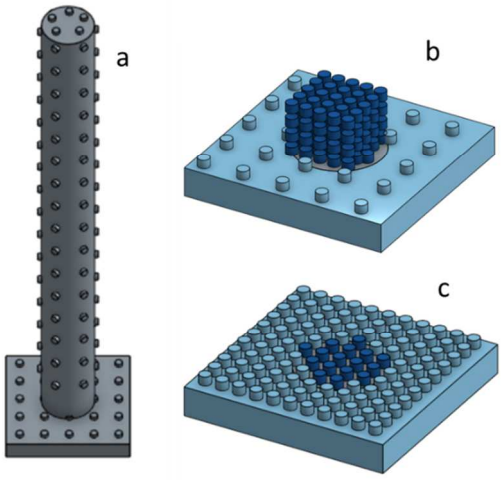

Figure S1: CAD models of Si/Co-P photocathodes. **(a)** A uniform deposition of Co-P particles (small cylinders) onto a microwire-on-planar substrate leads to deposition predominately on the sidewalls. **(b)** Catalyst island equivalent of the structure in (a), where catalysts loaded in the μW cross section are shaded. This approach is equivalent to a catalyst "island" strategy in which the surface area of the island is no longer constrained. **(c)** An equivalent loading of catalyst as in (b) on a standard planar substrate obscures the majority of the surface from incident sunlight.

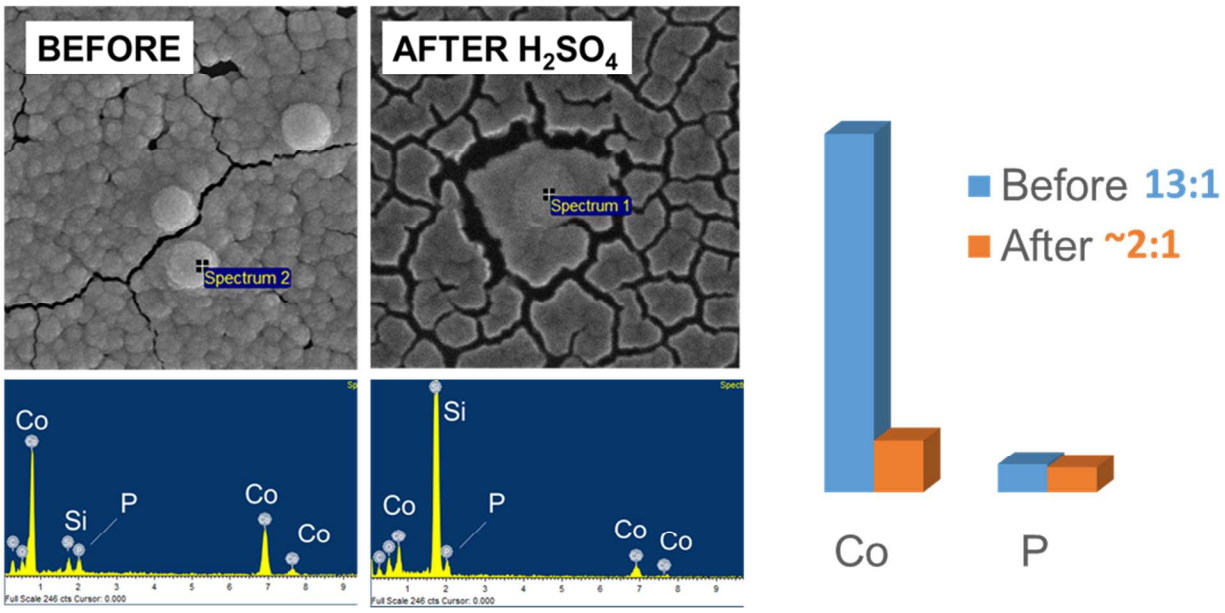

Figure S2: A comparison of the EDX spectra for an 800 mC cm^{-2} cathodic charge density passed Co-P film before and after testing showed a decrease in the intensity of the Co signal relative to the P signal. Additionally, the Si signal increased substantially relative to both the Co and P signals, consistent with an increased fraction of exposed Si.

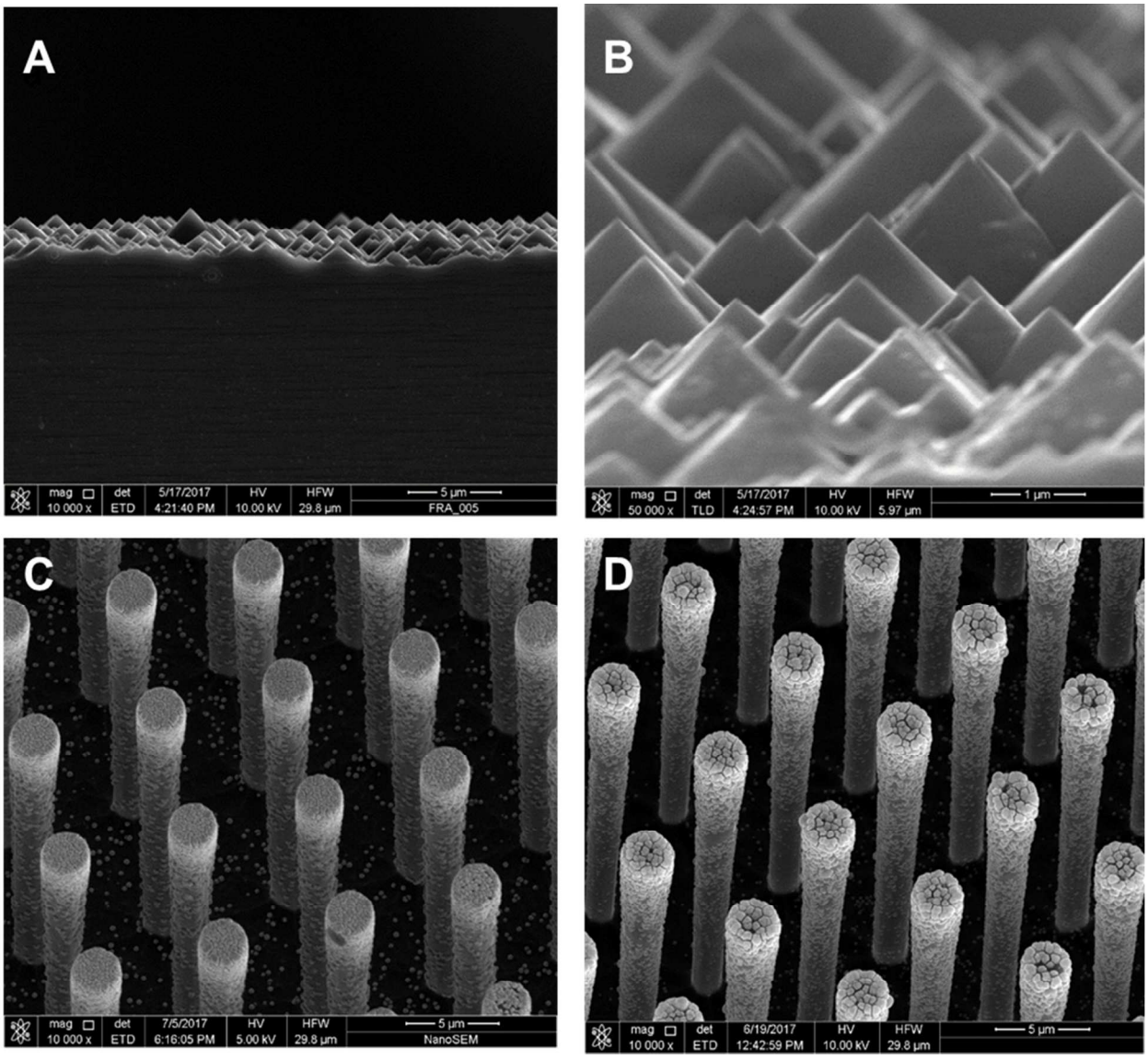

Figure S3: A) Bare µP surface on Si. **B)** µP structure at higher magnification showing a range of heights, but a consistent shape defined by the 54° angle between the Si <100> and <111> crystallographic planes **C)** n^+p-Si µW with 800 mC cm^{-2} Co-P. **D)** n^+p-Si µW with 1200 mC cm^{-2} Co-P. As the loading of Co-P was increased on the Si µWs, the thickness of the Co-P film on the wires increased, while the coverage of the planar substrate increased only marginally, showing that Co-P continued to be deposited in locations that would not contribute to parasitic absorption.

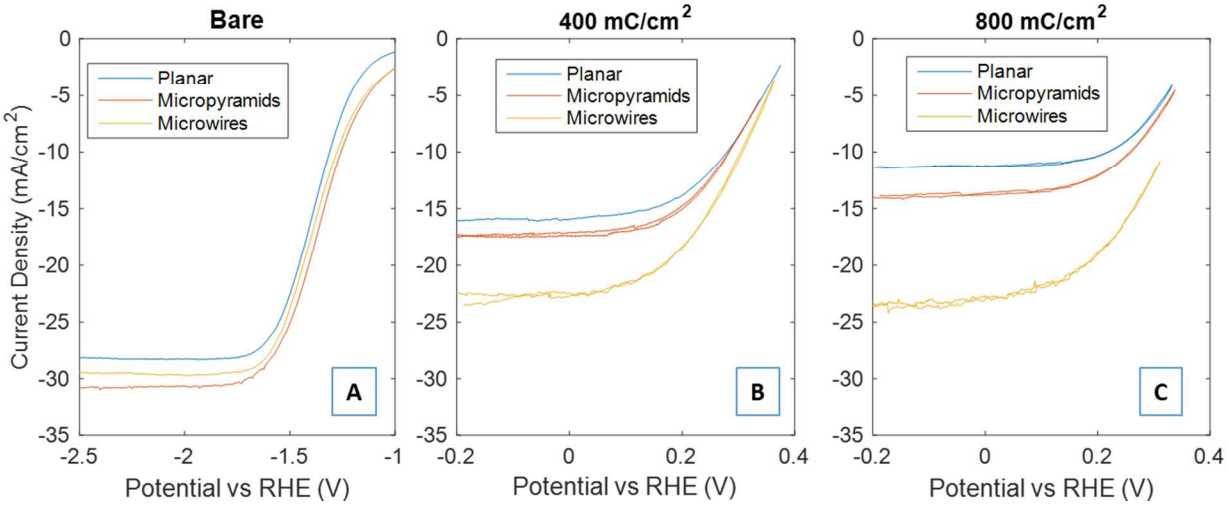

Figure S4: Representative *J-E* behavior for n^+-p Si photocathodes with Co-P in 0.50 M H_2SO_4(aq) under 100 mW cm^{-2} of simulated solar illumination, demonstrating the dependence of J_{sc} on catalyst loading. (A) For the bare n^+-p Si photocathodes, the potential was scanned at a rate of 200 mV s^{-1} from open circuit to a negative potential, allowing measurement of the light-limited photocurrent density in the absence of catalyst. Scans for the n^+-p Si/Co-P devices were recorded at 50 mV s^{-1} at potentials negative of the open-circuit potential to avoid oxidation of the Si/catalyst interface. The average J_{sc} (i.e. current density at 0 V vs RHE) decreased for planar and μP devices with increased catalyst loading, but remained unchanged for μW devices. (B,C) The average J_{sc} decreased for planar and μP devices with increased catalyst loading, but remained unchanged for μW devices.

Table S1: Average figures of merit for different p-Si and n^+p-Si structures loaded with Co-P and tested at 100 mW cm^{-2} of simulated sunlight in 0.50 M H_2SO_4(aq). The short-circuit current density, J_{sc} is the current density at the equilibrium potential for hydrogen evolution, RHE. The limiting current density, J_{lim}, was recorded at -0.3 V vs RHE and is proportional to the total number of photons collected by the underlying Si. These values are compared to the limiting current density recorded for the bare Si devices. The potential at -10 mA cm^{-2} and 0 mA cm^{-2}, as well as $V_{oc,}$ determined by the difference between the open-circuit potential and RHE, are also reported. Data points were recorded during scans at 50 mV s^{-1} after the device performance had stabilized.

Cathode structure	$\|J_{max}\|$ (mA cm^{-2})	Co-P loading = 400 mC cm^{-2}			
		$\|J_{sc}\|$ (mA cm^{-2})	V_{oc} (V vs RHE)	V_{10} (V vs RHE)	J_{sc}/J_{max}
p-Si/Co-P planar	27 ± 0.5	13 ± 1	0.265 ± 0.026	0.074 ± 0.010	0.51 ± 0.02
p-Si/Co-P μP	31 ± 2	18 ± 1	0.286 ± 0.011	0.181 ± 0.019	0.58 ± 0.05
p-Si/Co-P μW	28 ± 1	22 ± 2	0.342 ± 0.024	0.211 ± 0.012	**0.78 ± 0.05**

Cathode structure	$\|J_{max}\|$ (mA cm^{-2})	Co-P loading = 400 mC cm^{-2}				Co-P loading = 800 mC cm^{-2}			
		$\|J_{sc}\|$ (mA c m^{-2})	V_{oc} (V vs RHE)	V_{10} (vs RHE)	J_{sc}/J_{max}	$\|J_{sc}\|$ (mA c m^{-2})	V_{oc} (V vs RHE)	V_{10} (vs RHE)	J_{sc}/J_{max}
n^+p-Si/Co-P planar	28 ± 2	15 ± 4	430 ± 20	230 ± 40	0.58 ± 0.09	11 ± 3	430 ± 10	210 ± 10	0.39 ± 0.13
n^+p-Si/Co-P μP	32 ± 3	16 ± 4	430 ± 20	260 ± 30	0.50 ± 0.10	16 ± 2	420 ± 30	233 ± 58	0.49 ± 0.04
n^+p-Si/Co-P μW	31 ± 3	24 ± 1	460 ± 20	300 ± 20	**0.75 ± 0.04**	24 ± 4	420 ± 20	290 ± 24	**0.76 ± 0.06**

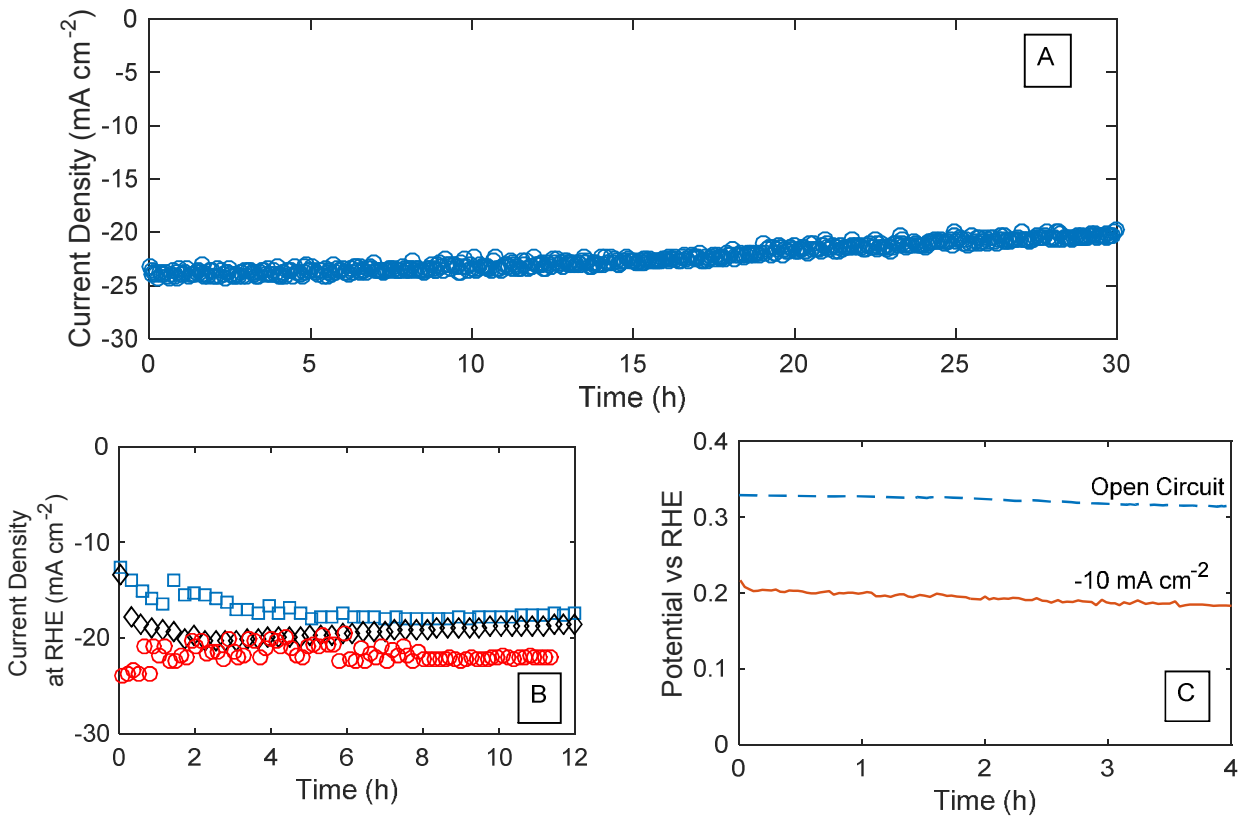

Figure S5: A) Chronoamperometry of a µW p-Si photocathodes with 400 mC cm^{-2} of Co-P in 0.50 M H_2SO_4(aq) under 100 mW cm^{-2} of simulated AM1.5G illumination. The light-limited current density was measured at -0.2 vs RHE and showed that parasitic absorption did not increase during device operation. B) Chronoamperometry of n^+p-Si µW (red circles), µP (black diamonds), and planar (blue squares) photocathode structures loaded with Co-P by passing 400 mC cm^{-2} of cathodic charge density. Current density at 0 V vs RHE (-0.231 vs Ag/AgCl) while in contact with 0.50 M H_2SO_4(aq) and under 100 mW cm^{-2} of simulated AM1.5G illumination. C) Chronopotentiometry of p-Si µW photocathode with 400 mC cm^{-2} Co-P under identical testing conditions as above. E_{oc}, the potential at open circuit versus RHE, and E_{10}, the potential required to reach -10 mA cm^{-2}, were stable over 4 hours of testing.

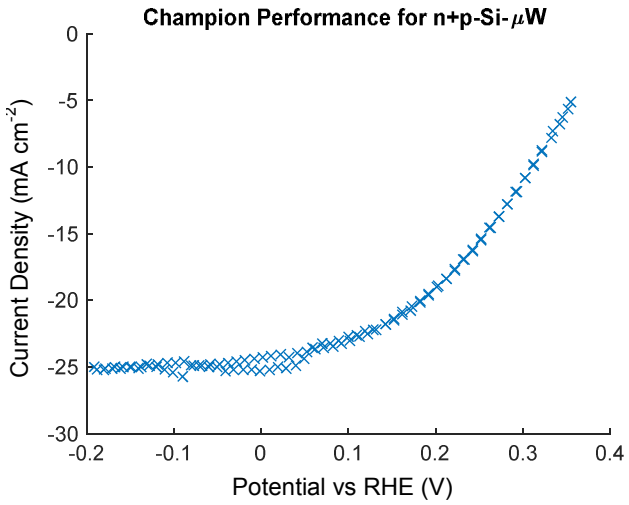

Figure S6: *J-E* behavior of the champion n^+p-Si-μW photocathode loaded with Co-P by passage of 400 mC cm^{-2} of cathodic charge density and tested under 1-Sun illumination in H_2(g)-purged 0.50 M H_2SO_4(aq). This device exhibited an open-circuit potential of +0.478 V vs RHE, a maximum J_{sc} (i.e current density at 0 V vs RHE) of 25.5 mA cm^{-2}, and a maximum power conversion efficiency of 3.95%.

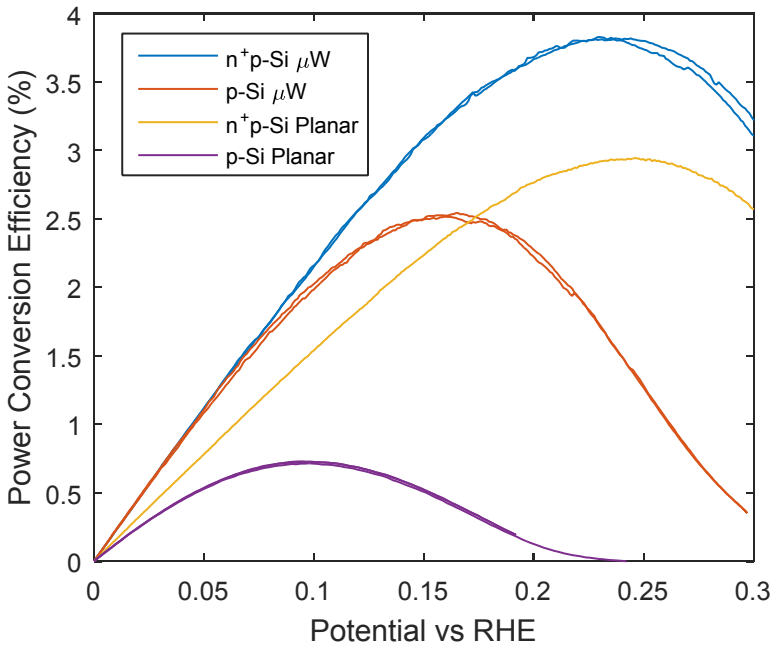

Figure S7: Power-conversion efficiencies for top-performing μW devices under 1 Sun illumination (100 mW cm^{-2}). The efficiency was calculated assuming 100% faradaic efficiency towards hydrogen evolution. n^+p-Si devices outperformed p-Si devices due to the increased voltage provided by the solid-state junction relative to the p-Si/liquid junction. The maximum efficiency of p-Si μW devices approached that of a planar n^+p-Si device, due to the more efficient catalyst utilization on the surface of the microstructured photocathode.

References

1. Bean, K. E., Anisotropic etching of silicon. *IEEE Transactions on Electron Devices* **1978,** *25* (10), 1185-1193.

2. Saadi, F. H.; Carim, A. I.; Verlage, E.; Hemminger, J. C.; Lewis, N. S.; Soriaga, M. P., CoP as an Acid-Stable Active Electrocatalyst for the Hydrogen-Evolution Reaction: Electrochemical Synthesis, Interfacial Characterization and Performance Evaluation. *The Journal of Physical Chemistry C* **2014,** *118* (50), 29294-29300.